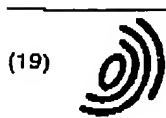


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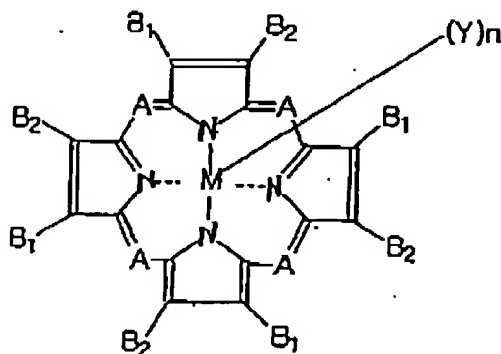
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(54) Organic electroluminescent device with improved long-term stability

(57) An organic electroluminescent device with improved long-term stability is disclosed, comprising either a dual layer of a layer I and a layer II or a mixture of the two layers between an EL multilayer and a cathode, the layer I being made of at least one alkali metal, alkaline earth metal, or its compound, the layer II being formed of at least one material selected from those having chemical formula I as shown below.

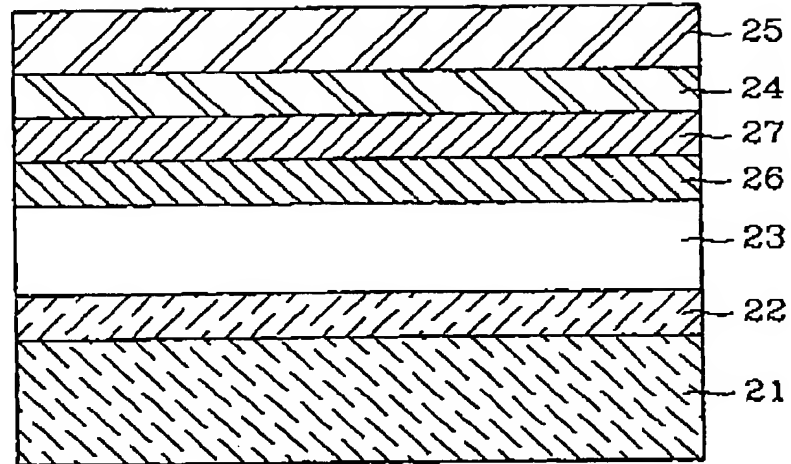
CHEMICAL FORMULA I



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FIG.2



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## Description

BACKGROUND OF THE INVENTION5 Field of the Invention

[0001] The present invention relates to a display, and more particularly, to an organic electroluminescent (EL) device.

10 Discussion of the Related Art

[0002] Organic EL devices, also called organic light emitting diodes (LEDs), are becoming very popular because of their possible application to flat panel displays (FPDs). They are extremely thin, matrix-addressable and operable at a relatively low voltage, typically less than 15 volts. Furthermore, they have additional features suitable for next generation FPDs such as, among other things, little dependence on viewing angle and good device-formability on flexible substrates. Organic LEDs differ fundamentally from conventional inorganic LEDs. While the charge transfer in inorganics is band-like in nature and the electron-hole recombination results in the interband emission of light, organic films are generally characterized by the low-mobility activated hopping transport and the emission is excitonic. Organic EL devices are also substantially different from conventional inorganic EL devices, especially in that organic EL devices are operable at low DC voltages.

20 [0003] Referring to Fig. 1, a typical organic EL device is provided with an anode 2 formed on a transparent substrate 1, a hole injecting layer (HIL) 3 and a hole transporting layer (HTL) 4 formed on the anode 2, a luminescent layer 5 formed on the HTL 4, an electron transporting layer (ETL) 6 and an electron injecting layer (EIL) 7 formed on the luminescent layer 5, and a cathode 8 formed on the EIL 7. Any one or more of HIL, HTL, EIL and ETL may be omitted, depending on the device structure adopted.

25 [0004] Electrons and holes injected into the luminescent layer through the cathode 8 and the anode 2, respectively, recombine to decay radiatively. For most organic EL devices, the charge injection barrier is higher for electrons than for holes. It is well known that the electron injection barrier may be lowered by employing a low work function material for a cathode. But low work function materials are chemically reactive, which makes it difficult to use them for electrodes. Accordingly, the materials are often used as a cathode after being alloyed with one of more stable materials, as seen  
30 In the examples of Mg:Ag and Al:Li. However, the alloyed cathodes are still less stable, more costly to form, and more difficult to deposit in a uniform film, compared to aluminum. Even more serious problem often encountered with an alloyed cathode of Mg:Ag or Al:Li is frequent occurrence of cross talk or leakage current between pixels, which may be attributed to the diffusion of Mg or Li ion across organic layers. The problem can be much alleviated if one selects aluminum as a cathode material, but then one needs to find a way to improve its poor electron injecting capability. The  
35 electron injecting capability of a high work function cathode such as aluminum can be significantly enhanced by inserting a very thin layer (typically 0.3 nm - 1.0 nm) of an electrically insulating material such as LiF, MgF<sub>2</sub> or Li<sub>2</sub>O either between an aluminum electrode and the luminescent layer or between the aluminum electrode and ETL [IEEE Transactions on Electronic Devices, Vol. 44, No. 8, p 1245-1248(1997)]. Li<sub>2</sub>O is a particularly interesting material in that it is an electrically insulating material with a very low work function. The work function of alkali metals themselves is very  
40 low, and it becomes even lower when oxidized: for example, work function decreases from 2.1 eV for Cs to about 1 eV for Cs<sub>2</sub>O. Various alkali metal compounds have been reportedly used to form an insulating buffer layer for the purpose of lowering the electron injecting barrier: to name a few, Li<sub>2</sub>O, LiBO<sub>2</sub>, NaCl, KCl, K<sub>2</sub>SiO<sub>3</sub>, PbCl, and C<sub>2</sub>S O. Despite said improvement, the introduction of the insulating buffer layer poses a challenging new problem: deterioration of adhesion between an EL multilayer and aluminum, and consequent reduction of life time. Experimental results reveal  
45 evidences of poor adhesion either at the buffer layer/aluminum interface or at the EL multilayer/buffer layer interface, which is not too surprising when different characteristics of materials involved are taken into account. In short, the related art suffers from poor adhesion and short life time.

SUMMARY OF THE INVENTION

50

[0005] Accordingly, the present invention is directed to an organic electroluminescent device that substantially obviates one or more of the problems due to limitations and disadvantages of the related art.

[0006] An object of the present invention is to provide an organic EL device with a long life time as well as a high efficiency.

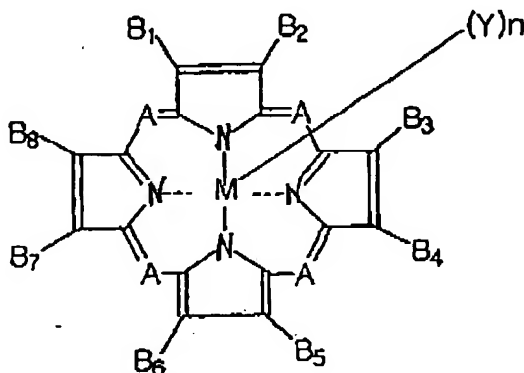
55 [0007] Additional features and advantages of the invention will be set forth in the description which follows, and in part will be apparent from the description, or may be learned by practice of the invention. The objectives and other advantages of the invention will be realized and attained by the structure particularly pointed out in the written description and claims hereof as well as the appended drawings.

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[0008] To achieve these and other advantages and in accordance with the purpose of the present invention, as embodied and broadly described, the organic electroluminescent device includes a layer I formed of at least one alkali metal, alkaline earth metal or its compound between an EL multilayer and a cathode formed of a metal or an alloy, and a layer II formed between the layer I and the EL multilayer. Here the EL multilayer means a plurality of layers comprising a luminescent layer and typically all or a part of HIL, HTL, ETL, and EIL.

[0009] In a preferred form of the invention, at least one porphyrinic compound forms the layer II which serves principally to improve the adhesion between the layer I and the EL multilayer while keeping a good electron transporting capability. Preferred porphyrinic compounds are those of structural formula I as shown below:

# CHEMICAL FORMULA I



wherein

A each independently denotes  $-N=$  or  $-C(R)=$ ;

R is hydrogen, alkyl, alkoxy, aralkyl, alkaryl, aryl, or heterocyclic group;

M is an element selected from IA, IIA, IIIA and IVA groups, and the third, fourth, fifth and sixth period groups in the periodic table;

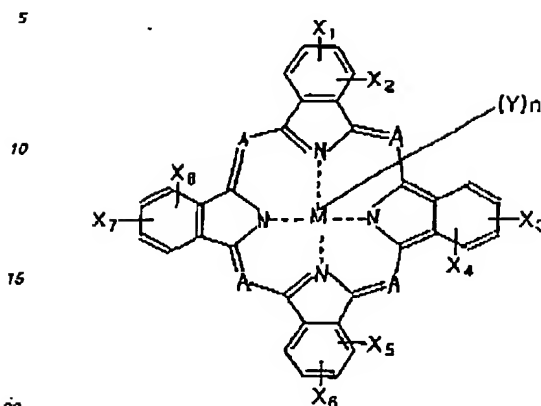
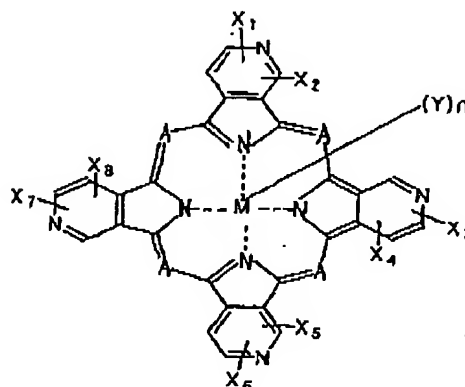
Y is a material chosen from alkoxy, phenoxy, alkylamine, arylamine, alkylphosphine, arylphosphine, alkylsulphur, and arylsulphur groups, and an element selected from VIA and VIIA groups in the periodic table;

n is an integer of 0, 1, or 2; and,

$B(B_1 \sim B_8)$  each independently represents hydrogen, alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, alkylthiol, arylthiol, nitroalkyl, alkylcarbonyl, alkoxy carbonyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen, or heterocyclic group, or together completes an unsaturated or saturated five, six, or seven-membered ring, which can include substituents such as alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, nitroalkyl, alkylcarbonyl, alkoxy carbonyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen, or heterocyclic group. Preferred five, six, or seven-membered rings are those formed of carbon, sulfur, oxygen and nitrogen ring atoms.

[0010] Highly preferred examples of useful porphyrinic compounds are phthalocyanines. Exemplary preferred materials are those of structural formulas II and III as shown below:

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CHEMICAL FORMULA IICHEMICAL FORMULA III

wherein

A each independently denotes -N= or -C(R)=;

R is hydrogen, alkyl, alkoxy, aralkyl, alkaryl, aryl, or heterocyclic group;

M is an element selected from IA, IIA, IIIA and IVA groups, and the third, fourth, fifth and sixth period groups in the periodic table;

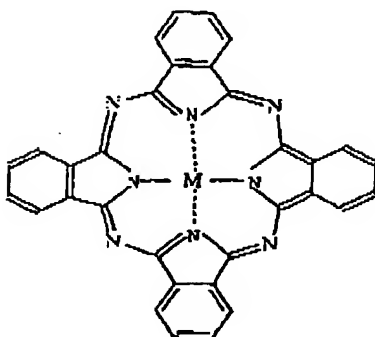
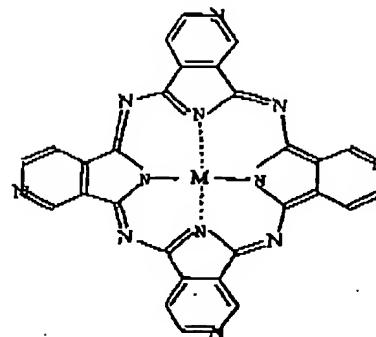
Y is a material chosen from alkoxy, phenoxy, alkylamine, arylamine, alkylphosphine, arylphosphine, alkylsulphur and arylsulphur groups, and an element selected from groups, and VIA and VIIA groups in the periodic table;

n is an integer of 0, 1, or 2; and,

X(X<sub>1</sub> ~ X<sub>8</sub>) each independently represents hydrogen, alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, alkylthiol, arylthiol, nitroalkyl, alkylcarbonyl, alkoxy carbonyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen, or heterocyclic group, or together completes an unsaturated or saturated five, six, or seven-membered ring, which can include substituents such as alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, nitroalkyl, alkylcarbonyl, alkoxy carbonyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen, or heterocyclic group. Preferred five, six, or seven, membered rings are those formed of carbon, sulfur, oxygen and nitrogen ring atoms.

[0011] The most preferred examples of phthalocyanines are those of structural formulas IV and V as shown below:

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CHEMICAL FORMULA IVCHEMICAL FORMULA V

wherein

M is an element chosen from Co, AlCl, Cu, 2Li, Fe, Pb, Mg, SiCl<sub>2</sub>, 2Na, Sn, Zn, Ni, Mn, VO, 2Ag, MnCl, and SnCl<sub>2</sub>.

[0012] In the other aspect of this invention, there is provided a means to improve the life time as well as the electron injecting capability by inserting, instead of a dual layer of the layer I and the layer II, a mixture of the two layers between the EL multilayer and the cathode. The mixed layer is formed by the co-deposition of (1) at least one alkali metal, alkaline earth metal, or its compound and (2) at least one porphyrinic compound. The mixing ratio between the two groups of materials can be fixed or varied as a function of position.

[0013] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory, and are intended to provide further explanation of the invention as claimed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The accompanying drawings, which are included to provide further understanding of the invention, and are incorporated in, and constitute a part of this specification, illustrate embodiments of the invention, and together with the description serve to explain the principles of the invention:

[0015] In the drawings:

Fig. 1 illustrates a cross-sectional view of a background art organic EL device; and

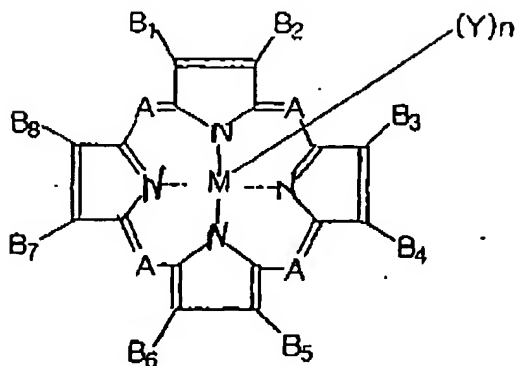
Fig. 2 illustrates a cross-sectional view of an organic EL device in accordance with a preferred embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0016] Reference will now be made in detail to the preferred embodiments of the present invention, an example of which is illustrated in the accompanying drawing. Fig. 2 schematically illustrates a sectional side view of an organic EL device in accordance with a preferred embodiment of the present invention.

[0017] Referring to Fig. 2, the organic EL device in accordance with a preferred embodiment of the present invention includes a laminated structure of a transparent substrate 21, an anode 22, an EL multilayer (typically of HIL, HTL, a luminescent layer, and ETL) 23, a cathode 24, and a protection film 25. Also inserted between the EL multilayer and the cathode are a layer I (27) and a layer II (26) which primarily serve for improving electron injection and adhesion, respectively. In a preferred form of the invention, at least one porphyrinic compound forms the layer II which serves principally to improve the adhesion between the layer I and the EL multilayer while keeping a good electron transporting capability. Preferred porphyrinic compounds are those of structural formula I as shown below:

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CHEMICAL FORMULA I

wherein

A each independently denotes -N= or -C(R)=;

R is hydrogen, alkyl, alkoxy, aralkyl, alkaryl, aryl, or heterocyclic group;

M is an element selected from IA, IIA, IIIA and IVA groups, and the third, fourth, fifth and sixth period groups in the periodic table;

Y is a material chosen from alkoxy, phenoxy, alkylamine, arylamine, alkylphosphine, arylphosphine, alkylsulphur, and arylsulphur groups, and an element selected from VIA and VIIA groups in the periodic table;

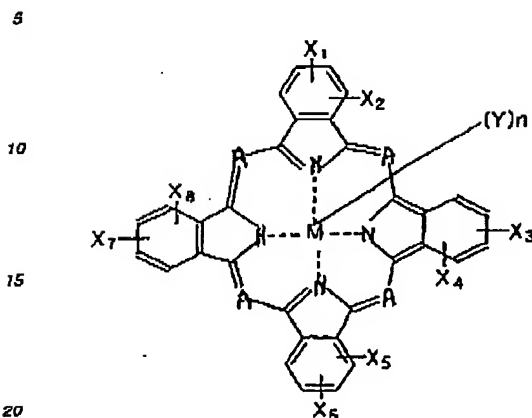
n is an integer of 0, 1, or 2; and

B(B<sub>1</sub> ~ B<sub>8</sub>) each independently represents hydrogen, alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, alkylthiol, arylthiol, nitroalkyl, alkylcarbonyl, alkoxy carbonyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen, or heterocyclic group, or together completes an unsaturated or saturated five, six, or seven-membered ring, which can include substituents such as alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, nitroalkyl, alkylcarbonyl, alkoxy carbonyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen, or heterocyclic group. Preferred five, six, or seven-membered rings are those formed of carbon, sulfur, oxygen and nitrogen ring atoms.

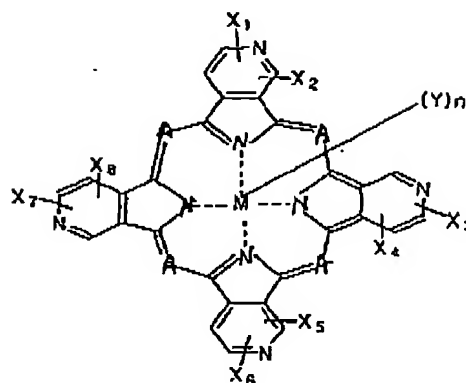
[0018] Highly preferred examples of useful porphyrinic compounds are phthalocyanines. Exemplary preferred phthalocyanines are those of structural formulas II and III as shown below:

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## CHEMICAL FORMULA II



## CHEMICAL FORMULA III



wherein

25 A each independently denotes -N= or -C(R)=;

R is hydrogen, alkyl, alkoxy, aralkyl, alkaryl, aryl, or heterocyclic group;

M is an element selected from IA, IIA, IIIA and IVA groups, and the third, fourth, fifth and sixth period groups in the periodic table;

30 Y is a material chosen from alkoxy, phenoxy, alkylamine, arylamine, alkylphosphine, arylphosphine, alkylsulphur, and arylsulphur groups, and an element selected from groups, and VIA and VIIA groups in the periodic table;

n is an integer of 0, 1, or 2; and

35 X(X<sub>1</sub> - X<sub>8</sub>) each independently represents hydrogen, alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, alkylthiol, arylthiol, nitroalkyl, alkylcarbonyl, alkoxy carbonyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen, or heterocyclic group, or together completes an unsaturated or saturated five, six, or seven-membered ring, which can include substituents such as alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, nitroalkyl, alkylcarbonyl, alkoxy carbonyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen, or heterocyclic group. Preferred five, six, or seven-membered rings are those formed of carbon, sulfur, oxygen and nitrogen ring atoms.

40 [0019] Preferentially, said M of chemical formulas I - III may be chosen from 2Li, 2Na, Mg, Tl, V, Cr, Mn, Fe, Co, Ni, Pt, Cu, 2Ag, Zn, Al, Ga, In, Si, Sn, Pb, and 2H, and said Y of chemical formulas I - III may be selected from oxygen, fluorine, chlorine, bromine, alkoxy group (alkyl moieties contain from about 1 to 10 carbon atoms), and phenoxy group.

[0020] The most preferred examples of phthalocyanines are those of structural formulas IV and V as shown below:

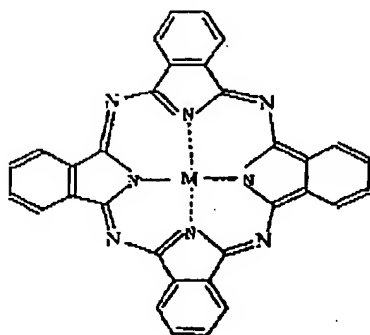
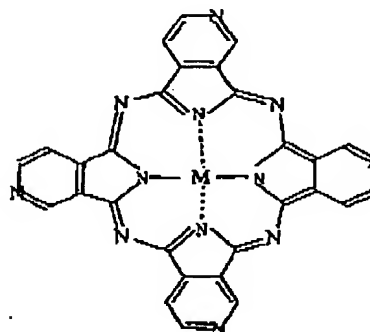
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CHEMICAL FORMULA IVCHEMICAL FORMULA V

wherein

M is an element chosen from Co, AlCl, Cu, 2Li, Fe, Pb, Mg, SiCl<sub>2</sub>, 2Na, Sn, Zn, Ni, Mn, VO, 2Ag, MnCl, and SnCl<sub>2</sub>.

[0021] The layer 1 (27) is designed to improve the electron injection capability and is formed of at least one alkali metal, alkaline earth metal, or its compound. Exemplary preferred materials are Li, Cs, Li<sub>2</sub>O, and LiF. The cathode 24 is formed of a metal or its alloy, and aluminum is most preferred.

[0022] The organic EL device of the present invention having the layer I (27) and the layer (26) thus stacked between the EL multilayer 23 and the cathode 24 shows a substantially prolonged life time as well as a high luminance. The layer (27) and the layer II (26) may be stacked in the opposite sequence, which however results in the decrease of luminance and life time. The layer I (27) and the layer II (26) may have a thickness of approx. 0.2 nm - 3 nm and 0.5 nm - 50 nm, respectively.

[0023] Exemplary devices have been fabricated in accordance with the present invention, and their performance has been compared with those of the background art: two devices of A and B are of the background art, and the other two devices of C and D are of the present invention. The basic device structure for green emission constitutes of (1) an anode of indium tin oxide (ITO) 150 nm thick, (2) a buffer layer of copper phthalocyanine (CuPc) typically 10nm - 20nm thick, (3) a hole transporting layer of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) typically 30nm - 50nm thick, and (4) an emitting layer of tris(8-hydroxy-quinolate)aluminum (Alq<sub>3</sub>) 40nm - 60nm thick. The device A has a cathode of aluminum formed directly on the EL multilayer (device structure: ITO/CuPc/TPD/Alq<sub>3</sub>/Al) while the device B has a layer of Li<sub>2</sub>O 1 nm thick between the EL multilayer and the cathode (ITO/CuPc/TPD/Alq<sub>3</sub>/Li<sub>2</sub>O (1nm)/Al). The device C has a structure of ITO/CuPc/TPD/Alq<sub>3</sub>/CuPc(2nm)/Li<sub>2</sub>O(1nm)/Al while the device D has a structure of ITO/CuPc/TPD/Alq<sub>3</sub>/Li<sub>2</sub>O(1nm)/CuPc(2nm)/Al. In short, the layer-forming sequence of Li<sub>2</sub>O(1nm) and CuPc(2nm) is reversed for the devices C and D. Finally, all devices have been encapsulated in an inert atmosphere.

[0024] TABLE I below lists the voltage measured between an anode and a cathode, luminance, and life time with the samples subjected to a constant current density of 3 mA/cm<sup>2</sup>.

TABLE I

	voltage (V)	luminance (cd/m <sup>2</sup> )	life time
Device A	6	50	short (less than 1 hour)
Device B	6	100	short (less than 1 hour)
Device C	6	150	long (longer than 2000 hours)
Device D	8	130	intermediate (roughly 100 hours)

[0025] The life time quoted in the above table represents the time by which luminance drops to half the initial value for each device. It is apparent in TABLE 1 that the devices C and D of the present invention are superior in the long-term stability to the devices A and B of the background art, which can be explained as follows. Li<sub>2</sub>O shows poor adhesion with both Alq<sub>3</sub> and aluminum. In addition, a 1 nm-thick layer of Li<sub>2</sub>O does not form a complete and uniform layer, but

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rather a kind of island structure. A part of the CuPc layer is apparently in direct contact with aluminum through the open space in the  $\text{Li}_2\text{O}$  layer, which significantly contributes to enhancing the adhesion of the organic/metal interface and consequently the life time of devices. The copper ion in CuPc is probably responsible for the relatively strong bonding between CuPc and aluminum. Compared to the device C, the device D exhibits a higher driving voltage because of the raised electron-injection barrier due to the presence of CuPc between  $\text{Li}_2\text{O}$  and aluminum, and consequently a shorter life time due to the increased electrical and thermal stress.

[0026] In the other aspect of this invention, there is provided a means to improve the life time as well as the electron injecting capability by inserting, instead of a dual layer of the layer I (27) and the layer II (26) in Fig. 2, a mixture of the two layers between the EL multilayer and the cathode. The mixed layer is formed by the co-deposition of (1) at least one alkali metal, alkaline earth metal, or its compound, and (2) at least one porphyrinic compound. The use of the mixed layer improves adhesion, but deteriorates electron injection slightly. The mixing ratio between the two groups of materials can be fixed or varied as a function of position, and the best performance has been obtained with (1) the relative concentration of the material(s) selected from a group of alkali metals, alkaline earth metals and their compounds being zero at the interface with the EL multilayer, and unity at the interface with the cathode, and varying gradually in between, and (2) the relative concentration of porphyrinic compound(s) being unity at the interface with the EL multilayer, and zero at the interface with the cathode, and varying gradually in between. The thickness of the mixed layer is in the range of 0.5 nm ~ 10 nm.

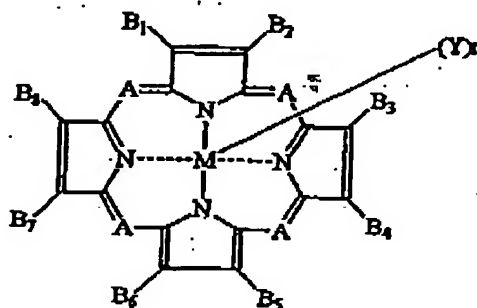
[0027] The organic EL devices of the present invention have the following advantages.

[0028] Inserting either a dual layer of a layer I and a layer II or a mixture of the two layers between the EL multilayer and the cathode helps to improve significantly the long-term stability as well as the luminance, with the layer II being formed of at least one material selected from those having chemical formula I, and with the layer I being made of at least one alkali metal, alkaline earth metal, or its compound.

[0029] It will be apparent to those skilled in the art that various modifications and variations can be made in the organic electroluminescent devices of the present invention without departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

## Claims

1. An organic electroluminescent (EL) device including at least one organic EL layer between a first electrode and a second electrode, said device comprising a layer formed of at least one porphyrinic compound.
2. An organic electroluminescent (EL) device as claimed in claim 1, wherein said porphyrinic compound has the structure of chemical formula 1 as shown below:

CHEMICAL FORMULA I

wherein:

A each independently denotes  $-\text{N}=\text{}$  or  $-\text{C}(\text{R})=\text{}$ ,

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R is hydrogen, alkyl, alkoxy, aralkyl, alkaryl, aryl or a heterocyclic group;

M is an element selected from IA, IIA, IIIA and IVA groups, and the third, fourth, fifth and sixth period groups in the periodic table;

Y is a material selected from alkoxy, phenoxy, alkylamine, arylamine, alkylphosphine,

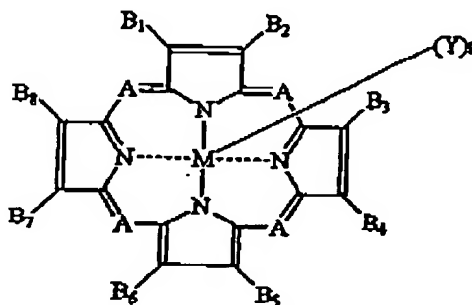
arylphosphine, alkylsulphur and arylsulphur groups, or an element selected from VIA and VIIA groups in the periodic table;

n is 0, 1 or 2; and

B<sub>1</sub>-B<sub>8</sub> each independently represents hydrogen, alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, alkylthiol, arylthiol, nitroalkyl, alkylcarbonyl, alkoxyalkyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen or a heterocyclic group, or two or more of which together complete an unsaturated or saturated five, six or seven-membered ring, which preferably includes one or more substituents selected from alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, nitroalkyl, alkylcarbonyl, alkoxyalkyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen and a heterocyclic group.

3. An organic electroluminescent (EL) device comprising, in sequence, a substrate, a first electrode, an EL multilayer, a layer II, a layer I, and a second electrode, wherein layer I is formed of at least one alkali metal, alkaline earth metal and/or compounds thereof, and layer II is formed of at least one material selected from those having chemical formula I as shown below:

#### CHEMICAL FORMULA I



wherein:

A each independently denotes  $-N=$  or  $-C(R)=$ ;

R is hydrogen, alkyl, alkoxy, aralkyl, alkaryl, aryl or a heterocyclic group;

M is an element selected from IA, IIA, IIIA and IVA groups, and the third, fourth, fifth and sixth period groups in the periodic table; Y is a material selected from alkoxy, phenoxy, alkylamine, arylamine, alkylphosphine, arylphosphine, alkylsulphur and arylsulphur groups, or an element selected from VIA and VIIA groups in the periodic table;

n is 0, 1 or 2; and,

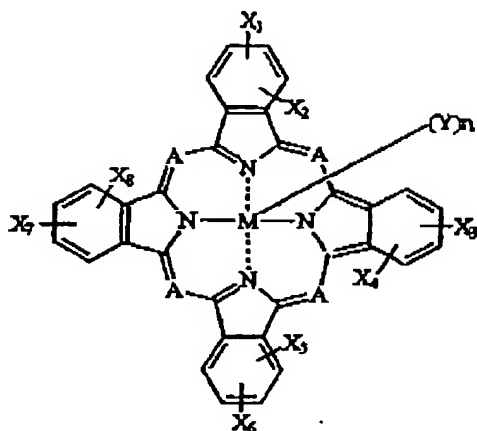
B<sub>1</sub>-B<sub>8</sub> each independently represents hydrogen, alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, alkylthiol, arylthiol, nitroalkyl, alkylcarbonyl, alkoxyalkyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen or a heterocyclic group, or two or more of which together complete an unsaturated or saturated five, six or seven-membered ring, which preferably includes one or more substituents selected from alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, nitroalkyl, alkylcarbonyl, alkoxyalkyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen and a heterocyclic group.

4. A device as claimed in claim 3, wherein layer I has a thickness of from 0.2 nm to 3 nm, and layer II has a thickness of from 0.5 nm to 50 nm.
5. A device as claimed in claim 3 or claim 4, wherein layer I is formed of  $Li_2O$ .

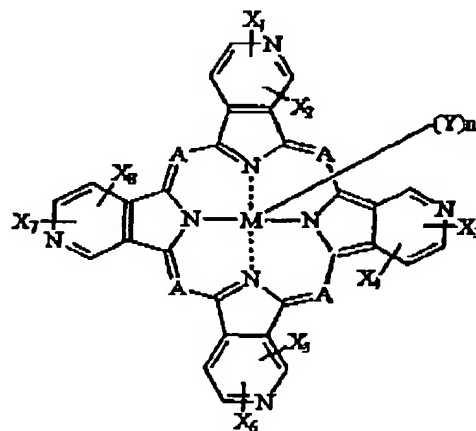
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6. A device as claimed in any one of claims 3 to 5, wherein layer II is formed of at least one material selected from those having chemical formulae II and III as shown below;

CHEMICAL FORMULA II



CHEMICAL FORMULA III



wherein:

A each independently denotes -N= or -C(R)=;

R is hydrogen, alkyl, alkoxy, aralkyl, alkaryl, aryl or a heterocyclic group;

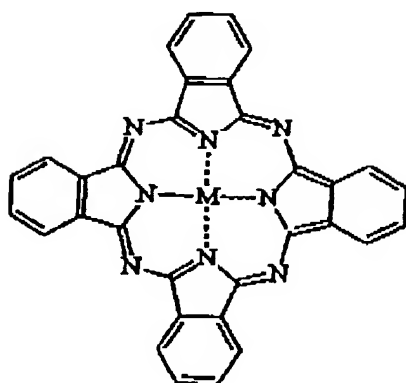
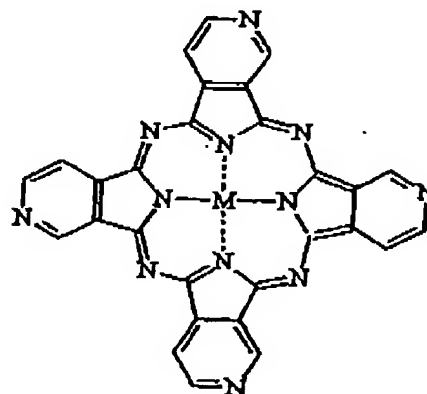
M is an element selected from IA, IIA, IIA and IVA groups, and the third, fourth, fifth and sixth period groups in the periodic table;

Y is a material selected from alkoxy, phenoxy, alkylamine, arylamine, alkylphosphine, arylphosphine, alkylsulphur and arylsulphur groups, or an element selected from groups VIA and VIIA groups in the periodic table; n is 0, 1, or 2; and,

X(X<sub>1</sub>~X<sub>8</sub>) each independently represents hydrogen, alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, alkylthiol, arylthiol, nitroalkyl, alkylcarbonyl, alkoxyalkyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen or a heterocyclic group, or two or more of which together complete an unsaturated or saturated five, six or seven-membered ring, which preferably includes one or more substituents selected from alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, nitroalkyl, alkylcarbonyl, alkoxyalkyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen and a heterocyclic group.

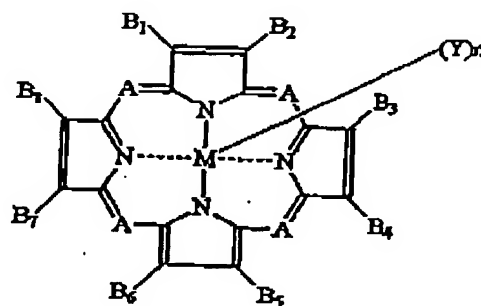
7. A device as claimed in any one of claims 3 to 6, wherein layer II is formed of at least one material selected from those having chemical formulae IV and V as shown below.

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CHEMICAL FORMULA IVCHEMICAL FORMULA V

wherein M is selected from Co, AlCl, Cu, 2Li, Fe, Pb, Mg, SiCl<sub>2</sub>, 2Na, Sn, Zn, Ni, Mn, VO, 2Ag, MnCl and SnCl<sub>2</sub>

8. An organic electroluminescent (EL) device comprising, in sequence, a first electrode, an EL multilayer, a mixed layer and a second electrode, wherein the mixed layer is formed by co-deposition of at least one material selected from a first group of alkali metals, alkaline earth metals and/or compounds thereof, and at least one more material selected from a second group of the materials having formula I:

CHEMICAL FORMULA I

wherein:

A each independently denotes -N= or -C(R)=;

R is hydrogen, alkyl, alkoxy, aralkyl, alkaryl, aryl or a heterocyclic group;

M is an element selected from IA, IIA, IIIA and IVA groups, and the third, fourth, fifth and sixth period groups in the periodic table;

Y is a material selected from alkoxy, phenoxy, alkylamine, arylamine, alkylphosphine, arylphosphine, alkylsulphur and arylsulphur groups, or an element selected from VIA and VIIA groups in the periodic table;

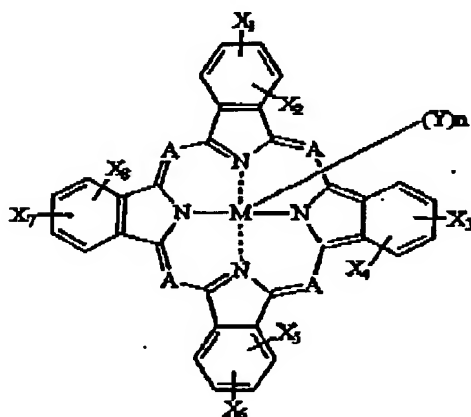
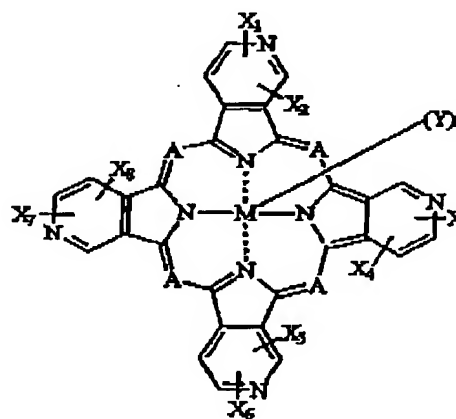
n is 0, 1 or 2; and,

B<sub>1</sub>(B<sub>1</sub>-B<sub>8</sub>) each independently represents hydrogen, alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, alkylthiol, arylthiol, nitroalkyl, alkylcarbonyl, alkoxyalkyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen or a heterocyclic group, or two or more of which together complete an unsatu-

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rated or saturated five, six or seven-membered ring, which preferably includes one or more substituents selected from alkyl, aryl, alkoxyl, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, nitroalkyl, alkylcarbonyl, alkoxycarbonyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen and a heterocyclic group.

- 5 9. A device as claimed in any one of claims 2 to 5 and 8, wherein two or more of B(B<sub>1</sub>-B<sub>6</sub>) together complete an unsaturated or saturated five, six or seven-membered ring formed of one or more of carbon, sulfur, oxygen and/or nitrogen atoms.
- 10 10. A device as claimed in any one of claims 2 to 5, 8 and 9, wherein said M of chemical formula I is selected from 2Li, 2Na, Mg, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Pt, Cu, 2Ag, Zn, Pd, Al, Ga, In, Si, Sn, Pb and 2H.
11. A device as claimed in any one of claims 2 to 5 and 8 to 10, wherein said Y of chemical formula I is selected from oxygen, fluorine, chlorine, bromine, an alkoxyl group (alkyl moieties contain from about 1 to 10 carbon atoms) and a phenoxy group.
- 15 12. A device as claimed in any one of claims 8 to 11, wherein the mixing ratio between said first and second groups of materials is either fixed or varied as a function of position.
13. A device as claimed in any one of claims 8 to 12, wherein the mixed layer has a thickness of from 0.5 nm to 10 nm.
- 20 14. A device as claimed in any one of claims 3 to 13, wherein the second electrode is formed of aluminium.
15. A device as claimed in any one of claims 8 to 14, wherein the material of the first group is Li<sub>2</sub>O.
- 25 16. A device as claimed in any one of claims 8 to 15, wherein the material of the second group is formed of at least one material selected from those having chemical formulae II and III as shown below:

CHEMICAL FORMULA IICHEMICAL FORMULA III

wherein:

A each independently denotes -N= or -C(R)=;

R is hydrogen, alkyl, alkoxyl, aralkyl, alkaryl, aryl or a heterocyclic group;

M is an element selected from IA, IIA, IIA and IVA groups, and the third, fourth, fifth and sixth period groups in the periodic table;

Y is a material selected from alkoxyl, phenoxy, alkylamine, arylamine, alkylphosphine, arylphosphine, alkylsulphur and arylsulphur groups, or an element selected from groups VIA and VIIA in the periodic table;

n is 0, 1, or 2; and,

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$X(X_1-X_8)$  each independently represents hydrogen, alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, alkylthiol, arylthiol, nitroalkyl, alkylcarbonyl, alkoxy carbonyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen or a heterocyclic group, or two or more of which together complete an unsaturated or saturated five, six, or seven-membered rings, which preferably includes one or more substituents selected from alkyl, aryl, alkoxy, aryloxyalkyl, hydroxyl, hydroxyalkyl, aralkyl, alkylamino, arylamino, nitroalkyl, alkylcarbonyl, alkoxy carbonyl, phenyl, amine, cyanyl, naphthyl, alkaryl, halogen and a heterocyclic group.

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17. A device as claimed in claim 6 or claim 16, wherein said M of chemical formulae II and III is selected from 2Li, 2Na, Mg, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Pt, Cu, 2Ag, Zn, Pd, Al, Ga, In, Si, Sn, Pb and 2H.

18. A device as claimed in any one of claims 6, 16 and 17, wherein said Y of chemical formulae II and III is selected from oxygen, fluorine, chlorine, bromine, an alkoxy group (alkyl moieties contain from about 1 to 10 carbon atoms) and a phenoxyl group.

19. A device as claimed in any one of claims 6 and 16 to 18, wherein two or more of  $X(X_1-X_8)$  together complete an unsaturated or saturated five, six, or seven-membered ring formed of one or more of carbon, sulfur, oxygen and/or nitrogen atoms.

20. A device as claimed in any one of claims 16 to 18, wherein the material of the second group is formed of at least one material selected from those having chemical formulae IV and V as shown below:

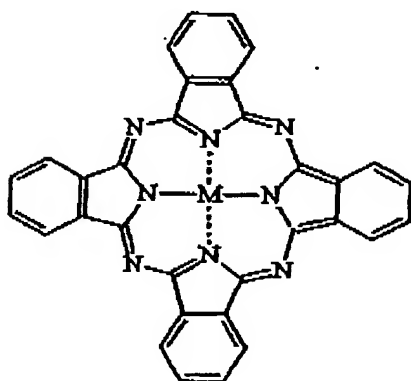
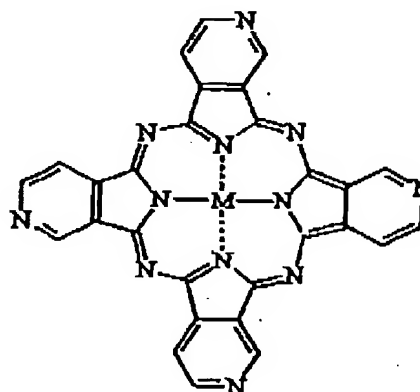
CHEMICAL FORMULA IV

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CHEMICAL FORMULA V

wherein:

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M is selected from Co, AlCl, Cu, 2Li, Fe, Pb, Mg, SiCl<sub>2</sub>, 2Na, Sn, Zn, Ni, Mn, VO, 2Ag, MnCl and SnCl<sub>2</sub>.

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FIG. 1  
Background Art

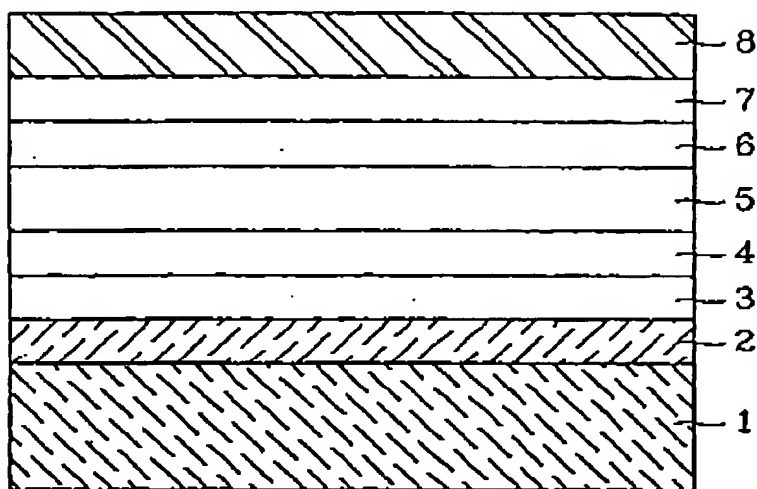
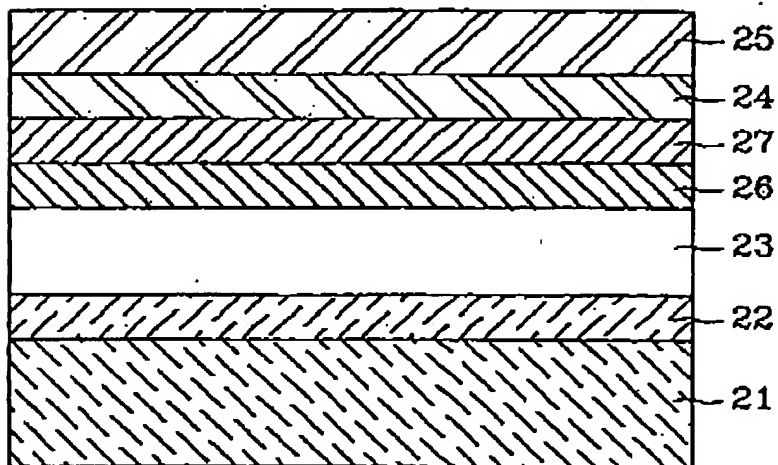
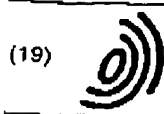


FIG. 2







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(11)

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(12)

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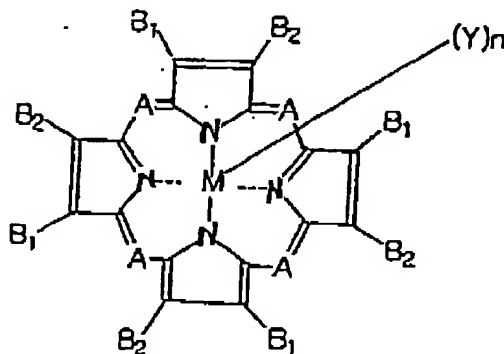
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(54) Organic electroluminescent device with improved long-term stability

(57) An organic electroluminescent device with improved long-term stability is disclosed, comprising either a dual layer of a layer I and a layer II or a mixture of the two layers between an EL multilayer and a cathode, the layer I being made of at least one alkali metal, alkaline earth metal, or its compound, the layer II being formed of at least one material selected from those having chemical formula I as shown below.

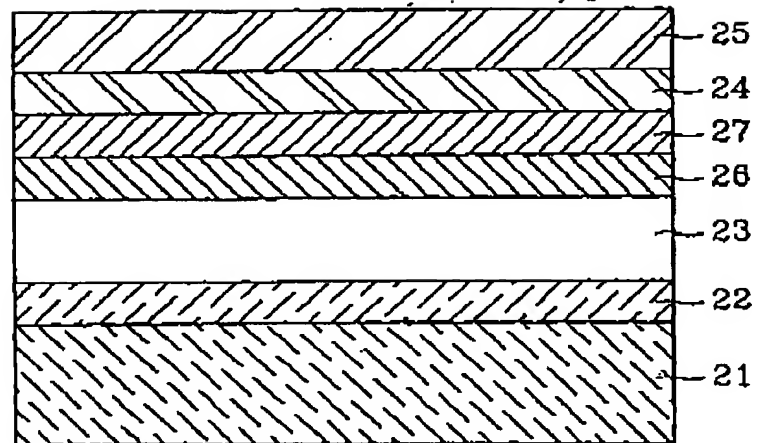
## CHEMICAL FORMULA I



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FIG.2



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## EUROPEAN SEARCH REPORT

Application Number  
EP 98 30 6710

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A		3-5	
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X	EP 0 704 915 A (OKI ELECTRIC IND CO LTD) 3 April 1996 (1996-04-03) * column 11, line 26-32; figure 6 *	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			H01L H05B
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>18 September 2000</b>	Examiner <b>De Laere, A</b>
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